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5≡ Purifying Method of Phenol	7≡ Inventor: Hwasaya Miki
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Detailed Description

1. Name of Invention

Purifying Method of Phenol

2. Scope of Patent Applied

1. A purifying procedure of crude phenol prepared by the cumene method, which features an extractive distillation by extracting part of the fraction without any extractive solvent from a distilling column that fractionally distills the mixture of the phenol and the extractive solvent, treats it with an acidic catalyst, and puts this acid-treated compound through stages of a high boiling-point substance removal procedure or a combination of the high boiling-point substance removal procedure and a hydroperoxide acid cleavage process.

2. A phenol purifying method described in Scope of Patent Applied Item 1 above, in which the fraction without any extracting solvent should amount to about 1 ~ 20 % by wt.(=by weight) when the total of purified phenol obtained would be 100 % by wt.

3. A phenol purifying method described in Scope of Patent Applied 1 above, which chooses a higher-boiling fraction over the fraction distilled to be about 1 ~ 20 % by wt. of the total purified phenol of 100 % by wt.

4. A purifying method of crude phenol prepared by the cumene method featuring the mixture of phenol and extracting solvent from the extractive distillation column, part of the fraction without having any extracting solvent extracted, treated with an acidic catalyst followed by distillation, then to circulate the acid-treated substance other than the purified phenol through a high boiling-point substance removal procedure or through stages of a high boiling-point substance removal procedure combined with a hydroperoxide acid cleavage process.

5. A purifying method of phenol described in Scope of Applied Item 4 above featuring the use of a fraction which would not contain extracting solvent at about 1 ~ 20 % by wt. for the total 100 % by wt. of the purified phenol obtained as the final product.

6. A purifying method of phenol described in Scope of Applied Item 4 above, featuring the use of a fraction without having any extracting solvent, its boiling temperature higher than

the fraction distilled at about 1 ~ 20 % by wt. of the total 100 % by wt. of purified phenol obtained as the final product.

3. Detailed Description of Invention

This invention refers to the purifying method of phenol. Precisely put, it refers to the purifying method of crude phenol prepared by the cumene method using an extractive distillation procedure.

It has been widely recognized that oxidation of cumene or cymene produces cumene-hydroperoxide or cymene-hydroperoxide, and when such product was made to cleave by an acidic catalyst and phenol products such as phenol, m-cresol and p-cresol were made, it was called the cumene method. These acid catalyst cleavage products were known as crude phenols, which were put through the normal distillation method. The fractioned phenol contains harmful impurities even though their solidifying point was so close to the theoretical solidifying point. When those impurities were sulfonated using concentrated sulfuric acid or treated with chlorine, the impurities can trigger undesirable coloring and the products were considered as not having high enough quality to meet the requirements.

There have been quite a few ideas and suggestions made on how to extract higher quality phenol from crude phenol made by the cumene method. One of them has been an extractive distillation method using polyalkylene-glycol or its ether, the impurities and unaffected portion being removed from the top of the distillation column, and then the extracted mixture being fractionated from the bottom of the column, and purified phenol being obtained through distillation. This method (Showa36-5713, JP Official Gazette) has been considered excellent from an industrial point of view; however, the impurities could not be totally removed by the extractive distillation.

Following is a detailed explanation of an extractive distillation method when crude phenol was the material to be processed. First, as shown in Drawing 1, cumene-hydroperoxide was made to cleave using an acidic catalyst, and the mixture was given some alkali for neutralization. Then the separated layers of water and oil were fed from Line 1 into column I for acetone removal. From the top of this column, low-boiling residues such as acetone were fractionated via Line 2, then led to an acetone-purifying column (not in Figure) to make purified acetone. On the other hand, residues at the bottom of the column were extracted by Line 3, after having removed low-boiling residues including acetone, which were supplied to the vacuum distillation column II. From the top of the vacuum distillation column, cumene and water would be taken away via Line 4, but a fraction of it could be returned to the vacuum distillation column via Line 5. The fraction containing phenol is extracted via Line 7. From the bottom of the vacuum distillation column, the fraction containing phenol would be extracted and fed to the distillation column III. From the bottom of the column III, substances with higher boiling temperatures than phenol would be removed via Line 8, and from the top, the fraction with crude phenol would be led to the extractive distillation column IV through Line 9. The placement of the vacuum distillation column (II) and the distillation column (III), which would come before the extractive distillation column, could be switched if desired.

The fraction supplied to the extractive distillation column could be fed to Line 10 again to have contact with polyalkylene-glycol counterflowing through Line 14, and the phenol extracted by this solvent, taken out from the bottom would be fed to the distillation column V via Line 11. The remaining impurities not extracted by the solvent would be taken from the top of the column IV and removed from the system flow via Line 12. Purified phenol distilled in this distillation column and fractionated from polyalkylene-glycol would be taken from the top of the column via Line 13 to become final products, while the extracting solvent would be taken from the bottom and circulated to the extractive distillation column IV via Line 14.

In this series of extractive distillation, although higher boiling substances than phenol could be mostly removed from the bottom of the distillation column, a fraction could remain and move up to the top of the distillation column little by little. Although some of these high boiling-point substances could be removed from the top of the extractive distillation column (IV), the remainder would come through the bottom of the distillation column along with the extracting solvent, and would be forwarded to the distillation column (V). This could cause unwanted accumulation of high boiling-point residues between the columns, eventually damaging the quality of what should be the purified phenol.

An attempt was made by the inventors to prevent accumulation of such high boiling-point substances by taking out a fraction without extracting solvent from the middle of the distillation column (V), feeding them back to columns I ~ III, and totally removing the high boiling substances from the bottom of the distillation column (III). It was learned, however, that this could not provide a solution, since long-term use of the distillation system could not stop the coloring substance from finding its way into the system.

The next attempt by the inventors was through applying the established methods to remove the coloring substance from crude phenol as described in Patent Publication #Sho(=Showa)39-622 and #Sho37-11664, which was to remove the coloring substance like benzofuran before getting into the distillation column, by applying a treatment using acidic catalyst. Unfortunately, however, it was learned that, due to a fraction of salt produced by the cumene-hydroperoxide neutralization, and also because of tar produced during the cumene-hydroperoxide acidic cleavage, exposure to acidic catalyst, such as the use of solid acid often preferred from an industrial standpoint, the solid acid's catalyst function was diminished too rapidly and the initial objective could not be accomplished.

From such experimental results it was found that, in order to obtain high-quality and steady phenol, a fraction not containing any extractive solvent needed to be extracted from the distillation column, which would fractionate phenol and extracting solvent, have it processed with acidic catalyst, and circulate the fraction as it was or after distillation.

This invention relates to a purifying method of crude phenol obtained by a cumene method, extracting a part of the fraction without any extracting solvent from the distillation column to fractionate the mixture of crude phenol and extracting solvent, treating it with an acidic catalyst, and returning the resulting oxidized fraction as it was, or, after putting it through distillation, returning it to the high boiling-point substances removal process, or to any point between such a process and hydroperoxide acidic cleavage procedure.

A fraction not containing any extracting solvent would indicate a content of extracting solvent generally less than about 1000 ppm, preferably less than about 500 ppm. Should the fraction contain a large amount of extracting solvent, it might cause undesirable results, such as partial change of extracting solvent at the time of contact with an acidic catalyst (i.e. oxidation changing diethylene glycol into dioxane), or the extracting solvent could be lost when the oxidized fraction needed to be returned to circulation during the high boiling-point substance removal process.

As the fraction not actually containing extracting solvent, the purified phenol fraction to become the final product could be used at about 1 ~ 20 % by wt. of the total 100 % by wt. of the final product obtained. However, it would be much preferred to use high boiling-point substances lower than the number of stages of the distillation column which distills the crude phenol fraction. Such higher-boiling fraction would generally be preferred to be about 1 ~ 20 % by wt., of the total 100 pts.wt of purified phenol fraction; however, the fraction supplied to the acid treatment process should ideally be about 3 ~ 15 % by wt. Should the extracted fraction amount be smaller, the purifying level would be less than satisfactory. On the other hand, should the fraction amount be larger, it would require more phenol for circulation or larger amount of phenol fraction would be put through the distillation of the acid-treated compounds. In either case the service load would be too large to justify from an economic viewpoint.

Acidic catalysts used for treating the fraction without containing any amount of extracting solvent would include sulfuric acid, hydrochloric acid, phosphoric acid; p-toluenesulfonic acid, phenol-sulfonic acid, trichloroacetic acid; solid acids, such as aluminum chloride, boron trifluoride or its ether-chain compounds; silica-alumina, activated clay, bentonite, montmorillonite and/or their acid-treated compounds like phosphoric-kieselguhr; acidic-ion exchange resins, such as sulfonic styrene and divinylbenzene. Among them solid acids would be ideal because of the ease of after-treatment. Although these acidic catalysts might vary depending on the type of catalysts or other conditions, about 0.005 ~ 10 wt.% of the entire fraction would be generally recommended to use. When treating continuously using a solid acidic catalyst as a fixed bed, the range of LHSV should be about 1 ~ 30, preferably within the range of about 3 ~ 10.

Although treatment with an acidic catalyst could be conducted intermittently, the preference would be the continuous method. It would be ideal to use the previously mentioned solid acid catalysts as the fixed bed and to conduct it continuously. The treatment temperature could be from room temperature to about 250°C, but the ideal range would be about 120°~180°C. In the case of phenol, for example, a higher temperature past its boiling point (181.8°C) would require pressure treatment. Treatment could be conducted in the environment with its pressure lower than atmospheric pressure. The length of the treatment should generally be about 1 ~ 60 minutes.

The fraction not containing extracting solvent treated with an acidic catalyst might be circulated immediately or after putting it through a distillation process, extracting purified phenol and making a phenol product from the top of the column. And the fraction in the bottom of the distillation column could be circulated.

The fraction at the bottom treated with an acidic catalyst or the fraction at the bottom put through the distillation process would be circulated through a removal process of high boiling-point substances or put through any stage between this process and the hydroperoxide acid cleavage process, but the preference would be to circulate the fraction through the removal process of high boiling-point substances.

As a result of this kind of treatment with an acidic catalyst, the boiling point of substances that caused coloring with similar boiling point and solubility to crude phenol, which could not have been totally removed by the extractive distillation, would become higher. Once that became the case, such substances treated with acid could be circulated through a high boiling-point substance removal process or other prior processes to remove the formulated high boiling-point substances. The substances that had been the cause of the coloring accumulated between the distillation column (IV) and the extractive distillation column (V) could then be removed, making it possible to obtain high-quality phenol, as desired.

As for the drawings to explain this invention, Drawing 2 would be a flow sheet showing a sequence of direct circulation of acid treated substances. Drawing 3 would also show a flow after distilling the acid-treated substances, and numbers III ~ V and 7 ~ 14 indicating the same items shown in Drawing 1.

The fraction of crude phenol supplied to the extractive distillation column III by Line 9 should preferably indicate the distillation operation in phases of acid-cleavage compounds removing low-boiling substances, i.e. acetone, cumene, α -methyl styrene and water; and high boiling-point substances, i.e. acetophenone, cumene-phenol, α -methylstyrenedimer, tar component and salt.

A polyalkylene glycol group item newly supplied by Line 10 and a polyalkyleneglycol item to be circulated via Line 14, as well as one or more of lower-grade polyalkylene glycol with a higher boiling point than phenol group ones, or their ether, i.e. diethylene glycol, triethylene glycol, dipropylene glycol, diethylene glycol methyl ether, diethylene glycol propyl ether and diethylene glycol butyl ether could be used. The amount used would depend on the amount of impurities in the crude phenol fraction or on desired quality level of purified phenol. Generally speaking, however, the fraction of crude phenol could be about 0.1 ~ 3 % by wt. and ideally should be about 0.3 ~ 1 % by wt.

The extractive distillation could take several operation methods depending on the type of phenol or the type of extracting solvent, but, in the case of phenol, it would be conducted under reduced pressure ranging from atmospheric pressure and about 10 mmHg (absolute pressure).

Most of crude phenol would be extracted by this extractive distillation operation via Line 11 from the bottom of the extractive distillation column (IV), and in case of phenol, most of the impurities including hydrocarbons such as cumene, α -styrene, acetophenone, mesityl oxide, 2-methyl-benzofuran, and hydroxyl acetone would be discarded from the system flow from the top of the column via Line 12.

Inside the distillation column V, crude phenol and the extracting solvent would be fractionated, purified phenol would come through Line 13, the fraction not containing any amount of extracting solvent would come from Line 15 (In case this fraction happened to be purified phenol, it should come from Line 13). Furthermore, extracting solvent should come from Line 14, containing a little bit of phenol, and each would be collected respectively. The purified phenol to be made into the final product would be treated during the distillation so that the content of extracting solvent within would be below the limit of detection (less than about 3 ppm) using gas chromatography. The fraction not containing any significant amount of extracting solvent would be put through the acid treatment apparatus (VI), then via Line 17, it would be returned to Line 8, the supply line to the distillation column (VII). Residues from the bottom of this column, which were high-boiling substances, would be discharged from the system flow (Drawing 2). The fraction not containing substantial extracting solvent would be treated by the acid treatment apparatus VI, circulated through Line 7 to be supplied to the (III) inside the distillation column (VII) via Line 16, while high boiling-point substances remaining at the bottom of the distillation column could be removed from the system flow via Line 18 (Drawing 3).

As for the distillation operation inside the distillation column (IV), impurities contained in crude phenol treated by the acid treatment apparatus (VI) had become high boiling-point substances allowing phenol fraction easier, if the distillation was constructed to prevent entrainment and whatever selected could be handled efficiently, making it possible to obtain purified phenol with a better sulfonation value via Line 17 at a recovery rate of about 70 ~ 95% under atmospheric pressure or reduced pressure environment. When this type of distillation operation might be added, a negative result of causing service loss could be added, such as heating the crude phenol twice in the distillation column III and V for purifying. The decision whether or not to add the extra procedure should be decided from a relative viewpoint of distillation cost in column VII vs. cost requirement for additional service.

Following are explanations of this invention using actual implemented examples.

Comparative Example

Following the format shown in Drawing 1, crude phenol prepared by the cumene method was purified using the extractive distillation method.

Using sulfuric acid dissolved the cumene hydroperoxide solution obtained by oxidizing cumene. The resulting acid-cleavage compound was neutralized by alkali, removed water, then fed into distillation column (I). Acetone and other lower-boiling fractions were removed and the fraction consisting of the following was obtained.

Phenol	56 wt.%
Cumene	15
Water	16
α -methyl styrene	6.0
Acetophenone	1.5
Carbinol	0.5
High boiling-point substances	5.0

When this fraction was supplied to vacuum distillation column (II) with 70 stages at 30 % by wt. every hour, pressure inside the column at about 200 mmHg, temperature at the top of column at 64°C, temperature at the bottom of the column at 178°C, and the distillation was conducted from the top water, cumene and other accompanying impurities were removed, and from the bottom, the fraction consisting of the following was removed.

Phenol	84 wt. %
Cumene	0.1
α -methyl styrene	3.2
High boiling-point substances	12.3

20 % by wt. of the above was taken out every hour, followed by the distillation of the phenol fraction in the distillation column (III) to remove high-point boiling substances.

This fraction of crude phenol was supplied to the center of the extractive distillation column (IV) of 54 stages at the speed of 17.5 pts.wt by the hour, and was to contact with counterflowing diethylene glycol, which was being circulated from the top of the column at 19.5-% by wt./ hour. The extractive distillation was conducted under the conditions of top of the column temperature at 92°C and bottom of the column temperature at 192°C. From the top, impurities that could not be extracted by diethylene glycol such as α -methyl styrene, cyclohexanol and ketone were removed, and from the bottom of the column, diethylene glycol solution, which had extracted phenol, was taken 36 % by wt. every hour, and supplied to the distillation column V. In this distillation column, distillation was carried out with the top of column temperature at 116°C, the 16.5 pts.wt of purified phenol was retrieved every hour and the sulfonation value was 85%.

This sulfonation value shown by the percentage was obtained as follows: First the sample phenol 20 ml was heated for 10 minutes above the warm water of 45°C, then concentrated sulfuric acid 20 ml was mixed in quickly, let stand at room temperature for 1 (one) minute, then let stand in water for 5 (five) minutes. The sample was moved into the 20 ml cell, and transmittance was measured by a photoelectric colorimeter at wavelength 532 m μ . It has been known that the larger the value, the better the quality.

Example 1

Following the formation given in Drawing 2 crude phenol prepared by the cumene method was purified using the extractive distillation method.

In the previous comparative example inside the column, from the supply stage that was 14 stages higher than the tray liquid phase, the fraction containing 275 ppm of diethylene glycol was extracted at the rate of 1 (one) % by wt. per 16.5 purified phenol extracted from the top of the column and put through the packing drum filled with activated clay (product by Japan Activated Clay, Nickel-Nite σ - 36, 30 ~ 60 mesh) of 0.17 capacity (1 capacity meaning 1 % by wt. was 1 ton equaling 1 m³) with the acid treatment conditions as follows. Substances thus treated with acid were mixed with substances supplied from the vacuum distillation column (7) and sent to the distillation column (III) for distilling operation, and high boiling-point substances were removed from the bottom of the column.

The crude phenol fraction free of high boiling-point substances was then supplied to the center of the extractive distillation column (IV) made of 54 stages 18.5 % by wt. every hour, and to have contact with counterflowing diethylene glycol brought in at the rate of 21 % by wt. per hour and which had been circulating as well. Extractive distillation was conducted in the same manner as the previous comparative example, phenol extracting diethylene glycol solution 38.5 pts.wt was retrieved from the bottom of the column and supplied to the distillation column (V) mentioned earlier. The distillation conducted inside the distillation column, while the top temperature was 116°C. Purified phenol was produced at the rate of 16.5 % by wt. by the hour at the top of the column. The sulfonation value of phenol thus obtained was measured.

Examples 2 ~ 7

In Example 1, the packing amount of activated clay into the packing drum (VI) was changed. By doing so, LHSV was adjusted, and treatment temperature was also changed in the purifying process.

Results obtained from Example 1 ~ 7 were shown in Chart 1 as follows.

Chart 1

Example	<u>Acid Treatment Conditions</u>		Purified Phenol Sulfonation Value (%)
	<u>LHSV (/hr)</u>	<u>Temperature (°C)</u>	
1	6	150	96
2	13	50	92
3	"	70	93
4	15	150	97
5	"	170	96
6	13	200	"
7	25	150	"

Example 8 ~ 11

Based on Example 1, acidic catalysts and other treatment conditions were changed for the purifying process, and the results obtained are seen in Chart 2 below.

Chart 2

Example	<u>Acid Treatment Conditions</u>			Purified Phenol Sulfonation Value (%)
	<u>Acidic Catalyst</u>	<u>LHSV (/hr)</u>	<u>Temperature (°C)</u>	
8	silica alumina	5	150	95
9	silica	"	"	"
10	activated clay	"	"	94
11	alumina	"	200	95

Example 12

The total of the fraction obtained from the bottom of the distillation column (II) at 20 % by wt. per hour as seen in the previous comparative example and the fraction circulated inside the distillation column (VII) at 0.2 % by wt. per hour amounting to 20.2-% by wt. per hour was

distilled in the distillation column (III), removing the high boiling-point substances, supplying the crude phenol fraction to extractive distillation column (IV), and force the countercurrent contact with circulating diethyl glycol brought at 20 pts.wt per hour into the top of the column. Impurities not extracted by extracting solvent were removed from the top of the extractive distillation column at the rate of 1.0 % by wt. per hour, while diethylene glycol solution having extracted phenol was coming from the bottom at the rate of 36.7 % by wt. per hour and was supplied to the distillation column (V). In this distillation column, purified phenol could be obtained from the top at the rate of 15.7 % by wt. per hour, and the sulfonation value of purified phenol thus obtained was 95%, which could become a product. These distillation-operating conditions were pretty much the same as those in the comparative examples.

While obtaining purified phenol at the rate of 15.7-% by wt. per hour as above, conditions were made to be the same as Example 1; in other words, removing high boiling-point substances at the rate of 1 % by wt. per hour, giving it a treatment with acid, the fraction was put into the distillation column (VII) (total 20 stages) with column top pressure at 135 mmHg, temperature 134 °C along with the bottom of the column temperature at 149 °C, and 0.8 % by wt. purified phenol was obtained every hour. The sulfonation value of this purified phenol was 98%, which could make a product phenol. The fraction at the bottom of this column was circulated back to the distillation column (III) at the rate of 0.2 % by wt./ hour as previously explained.

4. Overall Explanation of Drawings

Drawings were the flow sheets of a purifying method of crude phenol prepared by the cumene method, Drawing 1 showing the traditional style, and Drawing 2 ~ 3 showing the purifying method of crude phenol prepared by the cumene method using the method introduced by this invention.

In the Drawings, I = distillation column, II = vacuum distillation column, III = distillation column, IV = extractive distillation column, V = distillation column, VI = acid treatment apparatus, and VII = distillation column.

Represented by
Toshio Yoshida, Patent Attorney

Revised (voluntary)
Showa 56.11.13 (1981.11.13)

To: Director of Japan Patent Agency, Mr. Haruki Shimada

1. Relating Case Description

Showa Year 56 Patent Application No. 162, 192

2. Name of Invention

Purifying Method of Phenol

3. Revised by

Relationship to the matter: Applicant

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5. Portion of Contents Revised

[Scope of Patent Applied] portion in Detailed Description

6. Summary of Contents Revised

(1) [Scope of Patent Applied] will be revised as seen in the attachment.

(2) Page 6, Line 12 ~ 13:

[extractive distillation column – distillation column between] to be replaced by
[extractive distillation column (IV) – distillation column (V) between]

(3) Page 6, Line 14:

After [distillation column] add [(V)]

(4) Page 9, Line 4 from bottom:

Delete [TA RYUBUN TO SHI TE] (As the fraction)

(5) Page 15, Line 2:

Replace [about 3 ppm] with [about 30 ppm]

[Separate Sheet (Attachment)]

Scope of Patent Applied

1. A phenol purifying method featuring, in purifying crude phenol prepared by the cumene method using the extractive distillation method, to take out a portion of the fraction that does not contain any extracting solvent taken from the distillation column which would fractionate phenol and extracting solvent, treated with an acidic catalyst, this oxidized compound subjected to high boiling-point substance removal process or circulated at some stage between high boiling-point substance removal process and hydroperoxide acid cleavage process.

2. A phenol purifying method featuring as the fraction not containing any substantial amount of extracting solvent, the fraction used to obtain purified phenol as a product. The same fraction could be used as described in Scope of Patent Applied Item 1.

3. As described in Scope of Patent Applied Item 1, a phenol purifying method using the fraction with high boiling-point substance having a higher temperature than the fraction to obtain purified phenol as a product, as a fraction not containing a substantial amount of extra solvent to be taken out for an acidic catalyst treatment.

4. A phenol purifying method as described in Scope of Patent Applied Item 2 and 3. The weight ratio of removing amount of the fraction without containing substantial amount of extracting solvent would be about 1 ~ 20 % by wt. when the purified phenol obtained as a product would be 100 % by wt.

5. A phenol purifying method featuring, in purifying crude phenol prepared by the cumene method, the use of the extractive distillation method to take out a portion of the fraction without substantially containing any extracting solvent from the distillation column to separate the mixture of phenol and extracting solvent, have it treated with an acidic catalyst, distilling the oxidized compound, and sending the fraction other than the separated pure phenol to the process to remove high boiling-point substances or have it circulated at any point between that process and hydroperoxide acidic cleavage process.

6. A phenol purifying method described in Scope of Patent Applied Item 5, a fraction of purified phenol obtained as a product and the same fraction being used as a fraction not containing substantially any extracting solvent removed via acidic catalyst treatment.

7. A phenol purifying method described in Scope of Patent Applied Item 5, a fraction not containing any substantial amount of extracting solvent removed via acidic catalyst treatment. A fraction of high boiling-point substances with higher temperature than the fraction would be used to obtain purified phenol as a product.

8. A phenol purifying method described in Scope of Patent Applied Item 6 and 7. When the fraction of purified phenol obtained as a product would be 100 % by wt. the amount removed from the fraction without substantially containing extracting solvent would be about 1 ~ 20.